Stable Transition Metal−Enol Complexes in the Cycloheptatriene Ligand System

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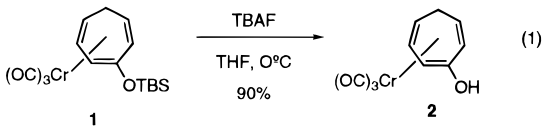
Complexation with transition metals is well-known to stabilize otherwise labile organic moieties. For example, transient species such as cyclobutadiene,[1] the dienone tautomer of phenol,[2] benzyne,[3] and cyclopentadienone[4] enjoy enhanced stability when complexed to appropriate transition metals. Stabilization of the enol form of the carbonyl keto−enol tautomeric system via metal complexation has also received attention, recently. To date, the bulk of these studies has dealt with structurally simple η^2-enol complexes prepared as isolable materials or as intermediates in various reaction pathways.[5,6] In contrast, stable metal−enol complexes involving greater hapticity in structurally more elaborate ligand systems appear to be quite rare.[7]

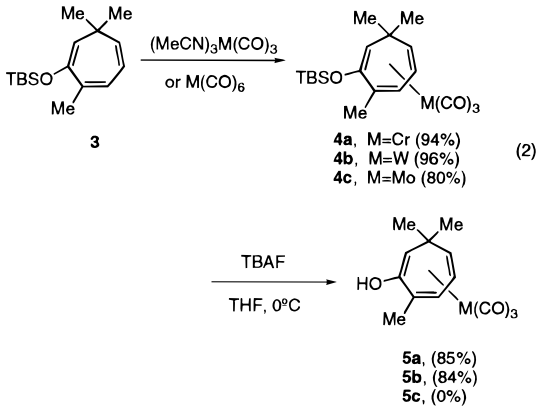
We now report on the preparation and reactions of several stable, isolable group 6 metal-based enol complexes derived from the cycloheptatriene ligand system. These species are easily accessed by fluoride ion induced desilylation of the corresponding [(trialkylsilyl)oxy]cycloheptatriene complexes. In a typical example, treatment of complex **1**[8] with anhydrous tetra-*n*-butylammonium fluoride in THF afforded the stable enol complex **2**[9] in 90% yield. Support for the enol structure



(1)

assigned to the red-orange complex **2** (mp 87−9 °C) was provided by infrared (3511 cm^{-1}) data as well as D_2O exchange experiments.[10a] The complex also gave satisfactory combustion analysis results.

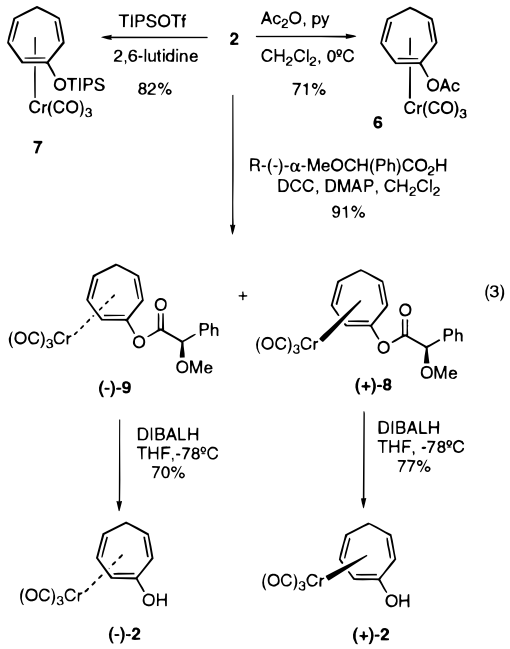
Structurally more elaborate enol complexes can also be prepared in the same fashion. Thus, exposure of the eucarvone-derived triene **3**[11] to either $(MeCN)_3M(CO)_3$ or $M(CO)_6$ afforded complexes **4a**−**c**[9] in good yields, and fluoride-mediated cleavage of the silyl ethers in the Cr(0) and W(0) species gave the corresponding, stable enol complexes **5a,b**[9,10b] in 85% and 84%



(2)

yields, respectively. In contrast, no enol complex could be identified when the molybendum-based complex **4c** was treated under identical conditions. This result is not particularly surprising since second-row transition metal π-complexes are frequently more labile than their first- and third-row counterparts.[12]

Although a number of metal−enol complexes have been prepared recently, very few reports regarding the chemical reactivity of these species (other than keto−enol tautomerism and H/D exchange) have surfaced.[7,13] As a consequence, few data are currently available concerning the utility of most enol complexes for subsequent derivatization of the hydroxyl function. It is noteworthy then that many of the metal−enol complexes reported in this document undergo smooth reaction to afford derivatives without compromising the integrity of the metal complex. For example, reaction of complex **2** with Ac_2O/pyridine in methylene chloride afforded the corresponding acetoxy complex **6** in 71% yield. Even more remarkable is the ease with which



(3)

the hindered triisopropylsilyl group can be installed onto enol

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(9) This compound exhibited spectral (^{1}H NMR, ^{13}C NMR, IR) and analytical (combustion analysis and/or HRMS) data consistent with those of the assigned structure.

(10) (a) Complex **2**: a broad singlet at 5.2 ppm is exchangeable with D_2O. b) Complex **5b**: a broad singlet at 4.2 ppm is exchangeable with D_2O.

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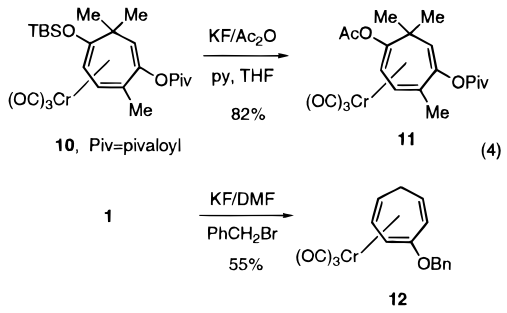
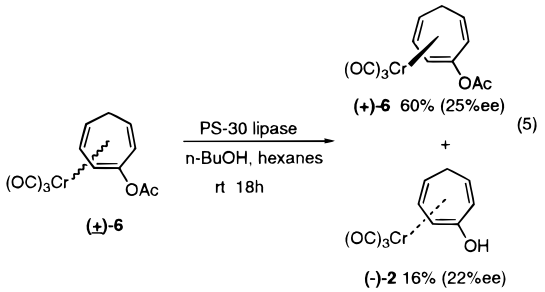
complex **2** employing conventional silylation conditions. Furthermore, the racemic mixture of enol complexes **(±)-2** can be acylated with (*R*)-(−)-α-methoxyphenylacetic acid in the presence of DCC in excellent yield and the resultant diastereomers conveniently separated. Careful reductive cleavage of the ester function in each of these diastereomers with DIBALH afforded the enantiomeric enol complexes **(+)-2** ($[\alpha]_D = +680°$) and **(−)-2** ($[\alpha]_D = -686°$) in *enantiomerically pure form* as determined by conversion into the corresponding Mosher esters.[14]

In an intriguing variation on this theme, direct derivatization of [(trialkylsilyl)oxy]cycloheptatriene complexes can also be achieved in good to excellent yields (eq 4). For example, the



highly substituted silyloxy species **10**[15] afforded the corresponding acetoxy complex **11** in excellent yield in the presence of KF under anhydrous conditions. It is noteworthy that O-alkylation prevails under these conditions when benzyl bromide is employed as the electrophilic agent in reaction with complex **1**. These desilylation results may afford some insight into the stability of the corresponding metal−enolate complexes, which are presumably involved as intermediates in these transformations.[16]

Biocatalytic resolution of these stable, metal−enol complexes represents a fascinating and synthetically appealing objective. Recent reports of enzymatic resolution of arene−chromium tricarbonyl complexes have appeared, but to the best of our knowledge no metal-stabilized enol complex has been successfully treated in this fashion.[17] In the event, exposure of **(±)-6** to Amano PS-30 lipase under conditions similar to those reported for organic substrates[18] afforded an easily separable mixture of enantiomerically-enriched **(+)-6** and **(−)-2** with



modest but encouraging efficiency. The experiment was taken to approximately 30% conversion, and the extent of resolution of enol complex **2** was established by comparison with enantiomerically pure **(−)-2** prepared previously. It is noteworthy that this particular enzyme appeared not to accept racemic **2** for the corresponding acylation process. Other lipases (from *Candida rugosa* and *Candida antartica* lipase B (Novo SP-435)) provided similar results. The ability to prepare enantiomerically enriched metal−enol complexes through enzymatic resolution appears to be unprecedented, and its successful implementation affords numerous opportunities for utilizing these complexes in organic synthesis.

In summary, several transition metal-stabilized hydroxycycloheptatrienes can be prepared and characterized. Furthermore, many of these enol complexes can undergo derivatization and biocatalytic resolution without significant demetalation. Applications for these stable metal−enol complexes in organic synthesis will be reported in due time.

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Supporting Information Available: Typical experimental procedures and complete spectroscopic data for all new compounds (9 pages). See any current masthead page for ordering and Internet access instruction.

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